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N.M.R. EVIDENCE FOR THE CONVERSION OF 4-[p-(2-CARBOXYETHYL)-PHENOXY]-2,4,6-TRI-t-BUTYL-2,5-, CYCLOHEXADIEN-1-ONE TO 2-[p-(2-CARBOXYETHYL)-PHENOXY]-4,6-DI-t-BUTYL PHENOL ON PYROLYSIS.

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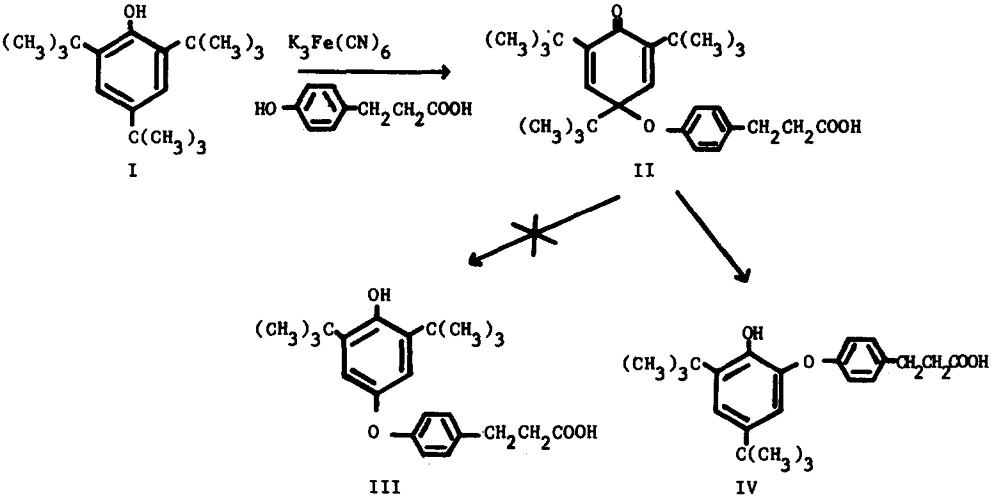
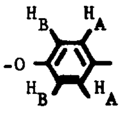
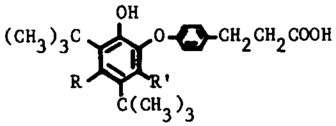
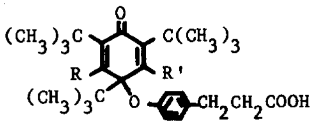
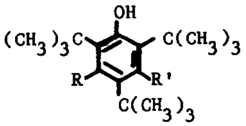
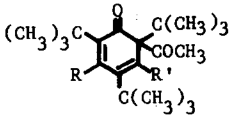
It has been reported (1) that 4-[p-(2-carboxyethyl)-phenoxy]-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (II) gives on pyrolysis 4-[p-(2-carboxyethyl)-phenoxy]-2,6-di-t-butyl phenol (III). In the course of work carried out at these laboratories this reaction was repeated and the product, although identical in physical properties to those given for (III), was found by nuclear magnetic resonance studies to be the corresponding ortho isomer (IV).



The N.M.R. spectrum of (IV; Table 1) was characterised by two singlets (each 9H) indicating non equivalent t-butyl groups and two doublets (each 1H) indicating non equivalent meta protons in the phenol.

TABLE 1

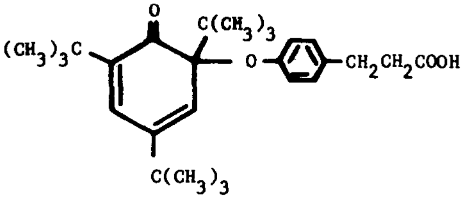
NO.	STRUCTURE	N.M.R. Absorption in τ*						
		$-C(CH_3)_3$	R=H	R'=H	$-CH_2CH_2-$	 HA	HB	$-CH_3$
IV		8.62 8.82	2.98(d) [J=2.5 c.p.s.]	3.27(d) [J=2.5 c.p.s.]	7.25 (m)	2.90(m)	3.14(m)	
II		8.81(18H) 8.93(9H)	3.28	3.28	7.27 (m)	2.96(m)	3.17(m)	
I		8.71(9H) 8.85(18H)	2.81	2.81				
V		8.85 8.78 9.07	3.13(d) [J=2.5 c.p.s.]	4.17(d) [J=2.5 c.p.s.]				7.97

* Spectra were recorded at 60 Mc./sec. (I,II and V) or 100 Mc./sec. (IV) for solutions in deuterochloroform (I,II and IV) or d_6-dimethylsulphoxide (V) with TMS as internal reference. Multiplicities are indicated by d, doublet; m, multiplet.

Structure (II) was also confirmed by N.M.R. as its spectrum showed three singlets; the first (2H) indicating equivalent meta protons in the cyclohexadienone ring, the second (18H) indicating equivalent ortho-t-butyl groups, and the third (9H) indicating the para-t-butyl group. The N.M.R. spectrum of (II) was also recorded in a variety of solvents e.g. deuterochloroform, d_5-pyridine, and d_6-dimethylsulphoxide and the t-butyl groups remained in the ratio 2:1 and the cyclohexadienone protons remained magnetically equivalent. 2,4,6-Tri-t-butyl phenol (I) also gave a spectrum with three singlets in support of structure (II).

Further proof for (II) followed from the preparation of 2-acetoxy-2,4,6-tri-t-butyl-3,5-cyclohexadien-1-one (V, Table 1) from the action of lead tetra-acetate on (I).(2) Comparison of the N.M.R. spectrum of this ortho-cyclohexadienone ether with that of (II) showed that the t-butyl groups were now in the ratio 1:1:1 and the cyclohexadienone protons were no longer magnetically equivalent.

As yet we have no evidence to suggest that the reaction mechanism involves a rearrangement to (VI) prior to loss of isobutylene.(3,4)



VI

Acknowledgement

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